

This Page Is Inserted by IFW Operations  
and is not a part of the Official Record

## **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

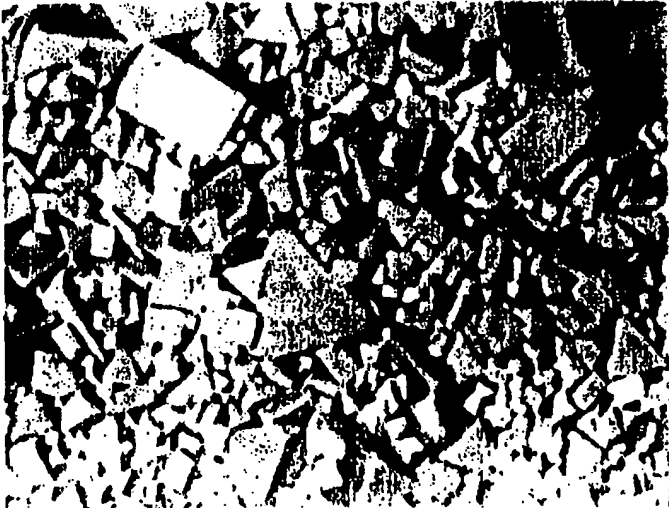
- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning documents *will not* correct images,  
please do not report the images to the  
Image Problem Mailbox.**

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>C04B 35/64 // C22C 29/08</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 98/02394</b> <b>(43) International Publication Date:</b> 22 January 1998 (22.01.98)
<b>(21) International Application Number:</b> PCT/SE97/01111 <b>(22) International Filing Date:</b> 23 June 1997 (23.06.97)  <b>(30) Priority Data:</b> 9602751-1 11 July 1996 (11.07.96) SE 9602752-9 11 July 1996 (11.07.96) SE  <b>(71) Applicant (for all designated States except US):</b> SANDVIK AB (publ) [SE/SE]; S-811 81 Sandviken (SE).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> ROHLIN, Barbro [SE/SE]; Vendevägen 25A, S-182 61 Djursholm (SE). PÄLSSON, Margareta [SE/SE]; Hökvägen 2, S-747 40 Gimo (SE). ÅKESSON, Leif [SE/SE]; Vågårdavägen 24, S-125 51 Älvsjö (SE).  <b>(74) Agents:</b> ÖSTLUND, Alf et al.; Sandvik AB, Patent Dept., S- 811 81 Sandviken (SE).		<b>(81) Designated States:</b> CN, IL, JP, KR, RU, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> SINTERING METHOD  <b>(57) Abstract</b> <p>The present invention relates to a method of sintering cemented carbide bodies including heating said bodies to the sintering temperature in a suitable atmosphere and cooling. If said cooling at least to below 1200 °C is performed in a hydrogen atmosphere of pressure 0.4-0.9 bar and &gt;0.1 bar noble gas, preferably argon cemented carbide bodies with no surface layer of binder phase are obtained. This is an advantage when said bodies are to be coated with wear resistant layers by the use of CVD-, MTCVD- or PVD-technique.</p> 		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

Sintering method

The present invention relates to a sintering method for cemented carbide for the purpose of eliminating the  
5 binder phase layer from its surface before applying coatings on said surface.

Coated cemented carbide inserts have now for many years been commercially available for chip forming machining of metals in the metal cutting industry. Such  
10 inserts are commonly made of a metal carbide, normally WC, generally with addition of carbides of other metals such as Nb, Ti, Ta, etc. and a metallic binder phase of cobalt. By depositing onto said inserts a thin layer of a wear resistant material such as TiC, TiN, Al<sub>2</sub>O<sub>3</sub> etc.  
15 separately or in combination it has been possible to increase the wear resistance at essentially maintained toughness.

During sintering cemented carbide inserts often obtain a completely or partly covering binder phase  
20 layer generally <1  $\mu$ m thick on their surface. This particularly applies to inserts with a binder phase enrichment in the surface below the coating, so called cobalt gradient but also to inserts with even distribution of binder phase. In the latter case this  
25 layer forms on certain grades but not on other. The reason to this is not understood at present. However, the layer has a negative effect on the process when carrying out CVD- or PVD-deposition, which results in layers with inferior properties and insufficient adherence. The binder phase layer must therefore be removed  
30 before carrying out the deposition process.

It is possible to remove such binder phase layer mechanically by blasting. The blasting method is, however, difficult to control. The difficulty resides in  
35 the inability to control consistently the blasting depth

with necessary accuracy, which leads to an increased scatter in the properties of the final product - the coated insert. It also results in damages to the hard constituent grain of the surface. However, in Swedish  
5 patent application 9202142-7 it is disclosed that blasting with fine particles gives an even removal of the binder phase layer without damaging the hard constituent grains.

Chemical or electrolytic methods could be used as  
10 alternatives for mechanical methods. US Patent 4,282,289 discloses a method of etching in a gaseous phase by using HCl in an initial phase of the coating process. In EP-A-337 696 there is proposed a wet chemical method of etching in nitric acid, hydrochloric acid, hydrofluoric  
15 acid, sulphuric acid and similar or electro-chemical methods. From JP 88-060279 it is known to use an alkaline solution, NaOH, and from JP 88-060280 to use an acid solution. JP 88-053269 discloses etching in nitric acid prior to diamond deposition. There is one drawback  
20 with these methods, namely, that they are incapable of only removing the cobalt layer. They also result in deep penetration, particularly in areas close to the edge. The etching medium not only removes cobalt from the surface but also penetrates areas between the hard constituent grains and as a result an undesired porosity between layer and substrate is obtained at the same time as  
25 the cobalt layer may partly remain in other areas of the insert. US 5,380,408 discloses an etching method according to which electrolytic etching is performed in  
30 a mixture of sulphuric acid and phosphoric acid. This method gives an even and complete removal of the binder phase layer without depth effect, i.e. reaching zero Co-content on the surface.

On the other hand it is in some cases not desirable  
35 to reach zero Co-content on the surface from coating

adhesive point of view, but rather a Co surface content close to nominal content.

The above mentioned methods require additional production steps and are for that reason less attractive for production in a large scale. It would be desirable if sintering could be performed in such a way that no binder phase layer is formed or alternatively can be removed during cooling.

It is therefore an object of the present invention to provide a method of sintering cemented carbide in such a way that no binder phase layer is present on the surface after the sintering process but a well defined Co content.

Figure 1 shows in 4000x magnification a top view of the surface of cemented carbide inserts partly covered with a binder phase layer. Figure 2 shows in 4000x magnification a top view of the surface of a cemented carbide insert sintered according to the invention. In these figures the dark grey areas are the Co-layer, the light grey angular grains are WC and the grey rounded grains are the so called gamma phase which is (Ti,Ta,Nb,W)C.

According to the method of the present invention the heating and high temperature steps of the sintering is performed in the conventional way. However, cooling from sintering temperature down to at least below 1200°C is performed in a hydrogen and argon atmosphere of 0.4 to 0.9 bar, preferably 0.5 to 0.8 bar pressure of hydrogen and rest argon. The total pressure shall be 0.5 to 100 bar, preferably 0.5 to 10 bar, most preferably 0.5 to 1 bar, the argon pressure always being >0.1 bar. The best conditions depend on the composition of the cemented carbide, on the sintering conditions and to a certain extent on the design of the equipment used. It is within the purview of the skilled artisan to determine by

experiments the optimum hydrogen pressure for which no binder phase layer is obtained and no undesired carburization of the cemented carbide is obtained. The sintering should lead to a Co content on the surface of nominal content  $+6/-4\%$ , preferably  $+4/-2\%$ . The Co content can be determined e.g. by the use of a SEM (Scanning Electron Microscope) equipped with an EDS (Energy Dispersive Spectrometer) and comparing the intensities of Co from the unknown surface and a reference, e.g. a polished section of a sample of the same nominal composition.

The method of the invention can be applied to all kinds of cemented carbides preferably to cemented carbide with a composition of 4 to 15 weight-% Co, up to 20 weight-% cubic carbides such as TiC, TaC, NbC etc. and rest WC. Most preferably the cemented carbide has a composition 5 to 12 weight-% Co, less than 12 weight-% cubic carbides such as TiC, TaC, NbC etc. and rest WC. The average WC grain size shall be  $<8\text{ }\mu\text{m}$ , preferably  $0.5-5\text{ }\mu\text{m}$ .

Inserts according to the invention are after sintering provided with a thin wear resistant coating including at least one layer by CVD-, MTCVD- or PVD- technique as known in the art.

The invention has been described with reference to argon but it is obvious that the same results can also be obtained with the use of other noble gases.

#### Example 1

Cemented carbide inserts of type CNMG 120408 with 5.5 weight-% Co, 8.5 weight-% cubic carbides and 86 weight-% WC of  $2\text{ }\mu\text{m}$  average WC-grain size were sintered in a conventional way at  $1450^{\circ}\text{C}$  and cooled to room temperature in argon. The surface was up to 50% covered with a Co-layer, Fig 1.

Inserts of the same composition and type were sintered in the same way but cooled from 1400 to 1200°C temperature in 0.5 bar hydrogen and rest argon and from 1200°C in pure argon atmosphere. The surface was to  
s about 6% covered with Co, which corresponds to the nominal Co content, Fig 2.



Claims

1. Method of sintering cemented carbide bodies including heating said bodies to the sintering temperature in a suitable atmosphere and cooling  
5 c h a r a c t e r i s e d in that said cooling at least to below 1200 °C is performed in a hydrogen atmosphere of pressure 0.4-0.9 bar and rest a noble gas, preferably argon, with a pressure of >0.1 bar with a total pressure of 0.5 to 100 bar, preferably 0.5 to 10 bar.
- 10 2. Method according to claim 1  
c h a r a c t e r i s e d in that said hydrogen pressure is 0.5-0.8 bar.
3. Method according to any of the preceding claims  
c h a r a c t e r i s e d in that said cemented carbide  
15 has the composition of 4 to 15 weight-% Co, up to 20 weight-% cubic carbides such as TiC, TaC, NbC etc. and rest WC.
4. Method according to any of the preceding claims  
c h a r a c t e r i s e d in that said cemented carbide  
20 has the composition 5 to 12 weight-% Co, less than 12 weight-% cubic carbides such as TiC, TaC, NbC etc. and rest WC.
5. Method according to any of the preceding claims  
c h a r a c t e r i s e d in that said bodies are  
25 provided with a thin wear resistant coating including at least one layer by CVD-, MTCVD- or PVD-technique.

1/1



Fig. 1

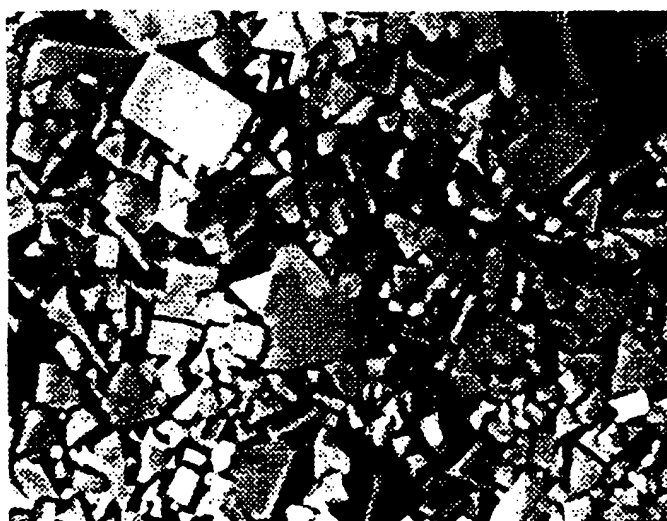


Fig. 2

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 97/01111

## A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C04B 35/64 // C22C 29/08

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C04B, C22C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

DIALOG: WPI, CLAIMS

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 9005200 A1 (KRUPP WIDIA GMBH), 17 May 1990 (17.05.90), page 2, line 32 - page 3, line 1  -- -----	1-5

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

## \* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

13 October 1997

Date of mailing of the international search report

23.11.1997

Name and mailing address of the ISA/  
Swedish Patent Office  
Box 5055, S-102 42 STOCKHOLM  
Facsimile No. +46 8 666 02 86

Authorized officer

May Hallne  
Telephone No. +46 8 782 25 00

**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

01/09/97

International application No.  
PCT/SE 97/01111

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9005200 A1	17/05/90	DE 3837006 A,C,R	03/05/90
		EP 0561768 A	29/09/93
		IN 172467 A	14/08/93
		JP 4501438 T	12/03/92
		US 5223020 A	29/06/93